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LOW-MELTING BOROSILICATE GLAZES FOR SPECIAL-PURPOSE AND CONSTRUCTION CERAMICS (A REVIEW)

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The properties and specific features of contemporary low-melting borosilicate glazes for special and construction purposes are given.

Low-melting borosilicate glazes are extensively used in the production of building materials. Materials whose surface is protected from the ambient medium and at the same time has good ornamental qualities enjoy a high demand lately. Such materials have become popular abroad. The challenge to be met by the Russian manufacturers is producing high-quality glazed ceramics for construction (facing brick, tiles, roof tiles). Therefore, revealing the regularities of the development of glaze formulas and preparation and production of low-melting glazes are topical problems.

A ceramic surface can be glazed by fritted or non-fritted low-melting borosilicate glazes, since B_2O_3 decreases melting temperature and increases the spreadability of glazes. Low-melting glazes contain water-soluble chemical compounds (soda, potash, saltpeter, borax, etc.). As glazes are deposited on ceramics in the form of aqueous suspensions, they are previously fused (fritted) at high temperatures for the purpose of transforming them into a water-insoluble state. Fritted glazes have a number of advantages over non-fritted ones. They are lasting, melt on articles at lower temperatures, and have higher quality. However, the production of fritted glazes raises energy consumption, which makes them more expensive than non-fritted raw glazes of the same compositions [1, 2].

A glaze for a particular ceramic base should be selected considering its TCLE and the melting point. One should also take into account data on viscosity (spreading), wettability, surface tension, and the evolution of the gaseous phase in glaze depending on increasing temperature.

The fusibility of the glaze should be coordinated with the sintering of the ceramic substrate. The glaze should become completely melted after the end of the reactions involving gas emission from the ceramic base and from the glaze itself. The fusibility of glaze depends on its viscosity and the quantity of the liquid phase in the melted glaze.

The main requirements imposed on glazes is the coordination between the TCLEs of glazes and ceramics. Only an insignificant difference (below 10%) in TCLE values is permissible. If the ceramic material has a higher TCLE, the glaze splits off in lumps. If the TCLE of the glaze is higher than the TCLE of the ceramic, the glaze in cooling develops cracks in the form of crackle.

A glaze appropriately selected for the particular ceramics substantially increases its mechanical strength. The ratio between the TCLEs of the glaze and ceramics is responsible for stress formation, which affects the thermal resistance and mechanical strength of the article.

Firing has a great effect on the strength of glazes. Unsatisfactory firing of a glazed product may produce crackle. Borosilicates formed at a high temperature partially dissolve the ceramic substrate; therefore, a zone of gradual transition from ceramic to glaze is formed at the site of contact of glaze with ceramics. If the firing duration is insufficient for the formation of this zone, the glaze is poorly bonded to the ceramic substrate. An excessive increase in firing temperature and duration makes the glaze dissolve too much of the ceramic substrate; consequently, the TCLE of the glaze changes and the glaze may exfoliate. An excessively abrupt cooling of glazed products after firing facilitates as well the formation of crackle.

The chemical composition of low-melting glazes varies within sufficiently large limits. The basic glaze contains silica, boron compounds, and alumina. Other oxides make up part of the glaze composition in small quantities but have a

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perceptible effect on the physicochemical properties of glazes. The most commonly used are alkali (K_2O, Na_2O) and alkaline-earth (CaO, MgO) oxides acting as fluxes. Oxides are introduced into glazes in the form of various minerals.

The compositions of low-melting glazes for construction ceramics and special purposes are listed in Table 1.

The glaze surface quality, its microstructure, and its physicochemical properties depend not only on its composition by also on the production method. The fineness of milling and slip consistency have great significance. Coarse milling of a suspension results in rapid precipitation of large particles and stratification of the suspension. It is established in research that insufficient milling of glazes increases its propensity to crackle.

The effect of oxides on glaze properties. The effect of various corrective additives and most frequently used oxides on the physiochemical properties of glaze should be taken into account in practice, when for production reasons glaze compositions have to be modified. The effect of each glaze component is not strictly proportional to the quantity introduced; this effect is frequently weakened depending on the total chemical composition of the glaze and the temperature and duration of firing.

Quartz SiO_2 raises the melting point, the viscosity of melted glaze, acid resistance, mechanical strength, and luster and decreases the TCLE. It is introduced in the form of quartz sand, pegmatite, and also makes up part of clay and kaolin.

Alumina Al_2O_3 raises the refractoriness and viscosity of the melt, improves chemical resistance, decreases the TCLE, and impedes good spreading of fritted glaze. It is introduced via clay, kaolin, feldspar, and calcined alumina.

Boron oxide B_2O_3 significantly decreases the melting point, increases leachability, improves luster, decreases the TCLE, and facilitates good spreading. It is introduced in the form of borax, boric acid, and calcium borate.

Lead oxide PbO is an intense flux facilitating an expansion of the melting interval, imparts a specially attractive luster, facilitates good spreading of glaze, and decreases the hardness and the TCLE of glaze. It is introduced in the form of minimum, white lead, and lead monoxide.

Sodium oxide Na_2O is an intense flux, which raises the TCLE, decreases fusibility and viscosity interval, lowers hardness, and improves the luster of glaze coating. It is introduced into the batch in the form of soda, borax, and sodium feldspar.

Potassium oxide K_2O is an intense flux, which increases the fusibility interval, improves luster, increases the TCLE, and is preferred to sodium oxide. It is introduced via orthoclase and potash.

Lithium oxide Li_2O is the most intense flux among the alkali oxides, which decreases viscosity, improves luster, and increases the TCLE. It is introduced into the batch via spodumene and lithium carbonate.

Calcium oxide CaO is the main flux for medium- and high-melting glazes. Its effect is weakly manifested in glazes with a melting point below 1150°C. Calcium oxide decreases the viscosity of the glaze melt with a high content of SiO_2 and increases hardness and strength. It is introduced in the form of chalk, marble, and opoka.

Magnesium oxide MgO is a stronger flux than CaO. It increases hardness, luster, strength, and elasticity of glaze coating. It is introduced in the form of opoka, talc, magnesite, and dolomite.

Barium oxide BaO is a flux. It decreases the TCLE and when introduced in a small amount improves the luster and mechanical properties of the glaze. It is introduced in the form of barium carbonate.

Zinc oxide ZnO is a good flux. It decreases the TCLE and facilitates the crystallization and opacification of glaze. It is introduced in the form of zinc white.

Strontium oxide SrO is a flux. It is used in low-melting glazes instead of PbO, has a positive effect on the firing interval, hardness, and chemical resistance, and improves luster. It is introduced with strontium carbonate.

Zirconium oxide ZrO_2 is an opacifier. It increases hardness and chemical resistance. It is introduced in its pure form or as zircon, which is itself an opacifier.

Tin oxide SnO_2 is a better opacifier, increasing chemical resistance, especially alkali resistance.

The effect of colorant additives on the color range of glaze coatings. Special colorant additives are introduced into glazes to obtain a color range for face surfaces of articles. Among the large number of different colorant additives, the most common are metal oxides mixed with other compounds and calcined at high temperatures. These colorants are tinted minerals. The most important are spinels $RO \cdot R_2O_3$ [RO) oxides of zinc, cobalt, manganese, magnesium, etc.; R_2O_3) oxides of aluminum, chromium, or iron]. When one of the components prevails, mixed crystals of spinel and excess oxide are formed, which imparts additional color shades to glazes.

The color of glaze depends not only on the colorant component but also on its concentration, glaze composition, and firing conditions. Therefore, for better display of the colors of some pigments, specials glaze compositions should be used.

The color of a glaze in general depends on its composition and the firing schedule of the glazed article. In compiling glaze formulas, one should bear in mind that finer milling of the glaze suspension, as well as introduction of sodium, potassium, magnesium, strontium and zinc oxides, contribute to improving luster.

A sharp decrease in luster and emergence of dullness on certain sites of a glazed surface may be due to the presence of a large number of craters on the glaze coating surface, or to crystallization of different new formations: cristobalite, feldspar, wollastonite, gypsum, calcium borate, etc. The emergence of craters can be attributed to the motion of fine gas bubbles from the depth of the glaze layer to its surface; many of such bubbles come up to the surface and burst. In

TABLE 1

Composition, wt.%	Properties	Specific features	Authors, published source
	Glazes for construction ceramics		
30 – 55 SiO_2, 10 – 25 B_2O_3, 0 – 5 Al_2O_3, 10 – 17 K_2O, 15 – 30 TiO_2, 0.05 – 3 Bi_2O_3, 0.1 – 0.3 Fe_2O_3, 0.1 – 3.5 SO_2, 0 – 2 carbon	Melting temperature 1000 – 1200°C Melting in reducing conditions	Black-color glaze, with 30 μm thickness has light transmission below 2%	G. Tiinker German patent No. 19605617
55.30 – 60.01 SiO_2, 11.34 – 11.82 Al_2O_3, 12.88 – 13.54 B_2O_3, 3.00 – 4.12 SrO, 3.02 – 4.91 CaO, 4.87 – 5.40 BaO, 4.03 – 5.47 Na_2O	Melting temperature 1300 – 1350°C Firing temperature 900 – 950°C TCLE $(40.7 – 43.01) \times 10^{-7}$ K^{-1} Thermal resistance 190 – 210°C	Decreased TCLE Increased thermal resistance Lustrous coating	N. M. Bobkova, E. A. Bukengol'ts, S. A. Gailevich USSR Inventor's Certif. No. 1097574
30.5 – 50.2 SiO_2, 12.5 – 23.0 B_2O_3, 2.5 – 9.0 Al_2O_3, 4.5 – 11.0 ZnO, 2.5 – 5.0 SrO, 5.8 – 9.8 Na_2O, 4 – 9 BaO, 4.2 – 8.5 ZrO_2	Melting temperature 1300 – 1330°C Firing temperature 800 – 830°C Firing duration 35 – 40 min TCLE $(63.8 – 68.7) \times 10^{-7}$ K^{-1}	Increased luster	O. G. Gorodetskaya, N. M. Bobkova, S. A. Gailevich, L. M. Silich USSR Inventor's Certif. No. 981270
62.7 – 65.0 SiO_2, 8.21 – 11.13 B_2O_3, 10.3 – 12.0 Al_2O_3, 0.20 – 0.38 Fe_2O_3, 2.0 – 2.5 K_2O, 10 – 13 Na_2O, 0.35 – 0.50 CaO, 0.2 – 0.4 MgO	Firing temperature 900 – 950°C Exposure at firing temperature 2 h	Increased thermal resistance and resistance to cold	O. I. Kvitsaridze, G. M. Kakabadze, G. S. Gverdtsiteli USSR Inventor's Certif. No. 966056
39.9 – 47.69 SiO_2, 33.68 – 39.52 B_2O_3, 0.51 – 0.59 Al_2O_3, 0.06 – 0.07 CaO, 10.32 – 10.68 MgO, 3.20 – 3.31 Na_2O, 3.19 – 3.31 K_2O	Firing temperature 780 – 1020°C TCLE 58.6×10^{-7} K^{-1} Thermal resistance 210 – 220°C Cold resistance 94 cycles	Increased firing interval Obtaining a purple-colored surface	K. K. Lukstan'sh, R. N. Berge, M. L. Grinberg, É. K. Avstinya USSR Inventor's Certif. No. 1066995
30.5 – 49.0 SiO_2, 9.0 – 15.2 B_2O_3, 4.5 – 14.6 Al_2O_3, 6.0 – 14.5 CaO, 3.6 – 7.0 MgO, 8.5 – 20.5 Na_2O, 7.0 – 15.0 TiO_2	Firing temperature 1050°C TCLE $(63 – 66) \times 10^{-7}$ K^{-1} Thermal resistance 5 – 6 thermal cycles	Increased thermal resistance Improved decorative properties	V. K. Baumane, V. K. Kaninya, G. V. Kalninysh, A. P. Raman, V. É. Shvinka, Yu. Ya. Éiduk USSR Inventor's Certif. No. 1058914
48.33 – 54.28 SiO_2, 4.40 – 8.39 B_2O_3, 12.74 – 19.12 Al_2O_3, 2.51 – 3.52 K_2O, 2.40 – 3.24 Na_2O, 12.50 – 22.87 CaO, 0.60 – 0.89 MgO, 2.08 – 2.16 Fe_2O_3	Firing temperature 920 – 1050°C TCLE $(63.2 – 66.4) \times 10^{-7}$ K^{-1} Glaze suspension density 1.52 g/cm^3 Cold resistance 100 cycles	Increased cold resistance Decreased TCLE Decreased firing duration	Yu. Kh. Popova, V. K. Levitskii, M. I. Popereka, B. G. Tishchenko, V. I. Akimov USSR Inventor's Certif. No. 1057452
57.36 – 58.08 SiO_2, 7.09 – 7.11 B_2O_3, 7.24 – 7.63 Al_2O_3, 2.54 – 1.73 K_2O, 3.72 – 4.39 Na_2O, 19.47 – 19.86 CaO, 1.34 – 1.54 MgO, 0.84 – 0.96 Fe_2O_3	Firing temperature 980 – 1100°C TCLE 69×10^{-7} K^{-1} Thermal resistance 200°C Luster 25% Whiteness 60% Cold resistance 50 cycles	Increased cold resistance, thermal resistance, whiteness Expanded firing interval	N. V. Kulikova, R. S. Krivosheeva, L. S. Opaleichuk, V. K. Tikhov, B. A. Morozov USSR Inventor's Certif. No. 1106796
20.68 – 23.10 SiO_2, 32.55 – 34.63 B_2O_3, 6.15 – 7.54 Al_2O_3, 9.96 – 10.61 PbO, 3.25 – 3.52 ZnO, 0.14 – 0.16 Fe_2O_3, 15.46 – 16.21 Na_2O, 0.75 – 0.78 K_2O	Melting temperature 950°C TCLE 67×10^{-7} K^{-1} Chemical resistance to water 98% Alkali resistance 84%	Obtaining dull glaze with high opacifying capacity	G. G. Gaprindashvili, E. Sh. Kharashvili, L. V. Mgaloblishvili, Z. A. Buishvili USSR Inventor's Certif. No. 592770
51.73 – 53.17 SiO_2, 8.43 – 9.08 B_2O_3, 3.87 – 6.16 Al_2O_3, 22.32 – 24.02 CaO, 1.27 – 1.38 MgO, 4.13 – 4.47 BaO, 0.15 – 1.15 K_2O, 2.89 – 4.47 Na_2O, 1.30 – 1.43 Fe_2O_3	Firing temperature 1000 – 1130°C TCLE $(52.9 – 53.1) \times 10^{-7}$ K^{-1} Thermal resistance 200°C Luster 50% Cold resistance 50 cycles	Decreased TCLE	N. V. Kulikova, I. V. Belkin, L. S. Opaleichuk, E. M. Aleksandrov USSR Inventor's Certif. No. 1025678

TABLE 1 (*continued*)

Composition, wt.%	Properties	Specific features	Authors, published source
64.48 – 66.92 SiO_2, 0.36 – 0.39 B_2O_3, 6.14 – 8.17 Al_2O_3, 2.87 – 3.25 CaO, 0.50 – 0.43 MgO, 1.47 – 2.25 K_2O, 11.12 – 12.66 Na_2O, 4.09 – 5.40 ZrO_2, 0.32 – 0.40 Fe_2O_3	Firing temperature 840 – 870°C TCLE (66.2 – 80.0) × 10^{-7} K^{-1} Thermal resistance 175 – 200°C Cold resistance 65 – 90 cycles	Increased cold resistance	M. I. Ryshchenko, N. G. Olifirenko, Yu. D. Trusova, G. V. Lisachuk, Yu. Kh. Popova USSR Inventor's Certif. No. 1100259
49.79 – 54.30 SiO_2, 7.11 – 8.19 B_2O_3, 11.71 – 13.60 Al_2O_3, 18.69 – 22.40 CaO, 2.22 – 2.58 K_2O, 2.13 – 3.00 Na_2O, 1.62 – 2.05 Fe_2O_3	Firing start temperature 880°C Firing end temperature 1100°C TCLE (6.16 – 6.76) × 10^{-7} K^{-1} Cold resistance 50 cycles	The glaze has lustrous surface without cracks and other defects Increased firing interval	Yu. A. Popova, E. L. Baranova, V. K. Levitskii, N. T. Krivonosova, B. G. Tishchenko, V. V. Knyazev USSR Inventor's Certif. No. 1025677
43.6 – 45.2 SiO_2, 21.4 – 23.6 B_2O_3, 5.9 – 8.1 Al_2O_3, 8.0 – 6.2 CaO, 1.9 – 3.8 BaO, 0.9 – 1.1 K_2O, 6.1 – 8.4 Na_2O, 3.9 – 7.3 ZrO_2, 3.3 – 3.9 F	Firing temperature 900°C TCLE 6.3 × 10^{-6} K^{-1} Thermal resistance 200°C Whiteness 80%	Decreased consumption of ceramic pigments	Z. N. Sofronova, N. E. Glozman, A. I. Ermolaeva, L. P. Bevzenko, M. É. Kats USSR Inventor's Certif. No. 1028616
31 – 36 SiO_2, 24 – 27 B_2O_3, 6 – 9 Al_2O_3, 2.5 – 5.0 ZnO, 2.0 – 5.5 K_2O, 2.0 – 5.5 Na_2O, 7 – 9 ZrO_2	Melting temperature 1250 – 1300°C Firing temperature 800 – 850°C TCLE (52.6 – 56.8) × 10^{-7} K^{-1} Whiteness 90% Luster 72 – 74%	Decreased TCLE Increased spreadability, degree of opacification, and luster	N. M. Bobkova, Z. V. Apanovich, S. A. Gailevich, I. M. Bykovets, Ya. I. Moiseeva USSR Inventor's Certif. No. 1102777
58.0 – 60.0 SiO_2, 13.0 – 14.0 B_2O_3, 13.9 – 16.0 Al_2O_3, 4.0 – 8.0 CaO, 2.0 – 6.0 MgO, 0.1 – 1.0 K_2O, 0.1 – 1.0 Na_2O, 13.0 – 14.0 TiO_2	Thermal resistance 12 – 20 thermal cycles Cold resistance 100 – 110 cycles	Increased cold resistance	O. A. Shchepochkina RF patent No. 2056380
47.35 – 57.85 SiO_2, 13.7 – 14.7 B_2O_3, 0.48 – 0.6 Fe_2O_3, 10.32 – 13.8 Al_2O_3, 13.25 – 1.46 CaO, 0.45 – 0.65 MgO, 1.3 – 2.0 K_2O, 1.32 – 2.10 Na_2O, 1.33 – 3.33 ZrO_2	Melting temperature 1300°C Firing temperature 850 – 1050°C Thermal resistance 250 – 275°C Cold resistance 55 – 60 cycles	Increased firing interval	G. M. Kakabadze, Ts. P. Tsanava, R. A. Mamaladze USSR Inventor's Certif. No. 1114639
52.0 – 54.0 SiO_2, 10.9 – 11.9 B_2O_3, 3.5 – 5.6 Al_2O_3, 13.5 – 16.0 CaO, 1.0 – 3.0 MgO, 6.0 – 7.0 K_2O, 0.1 – 1.2 Na_2O, 2.0 – 4.0 SO_2, 4.0 – 6.0 TiO_2	Melting temperature 1400°C Firing temperature 900°C Thermal resistance 20 thermal cycles Cold resistance 60 – 70 cycles	Increased cold resistance	O. A. Shchepochkina RF patent No. 2056381
33 – 48 SiO_2, 9.2 – 14.0 B_2O_3, 12 – 16 Al_2O_3, 1 – 3 Fe_2O_3, 0.8 – 5.0 SrO, 22 – 32 CaO, 0.5 – 3.0 MgO, 0.2 – 2.0 K_2O, 2.5 – 6.0 Na_2O	Firing temperature 980 – 1000°C Softening temperature 940 – 960°C Abrasion weight loss 0.025 – 0.02 g/cm^2	Increased crystallization capacity and abrasion resistance	K. K. Kvyatkovskaya, T. V. Rodionova, F. F. Savkin USSR Inventor's Certif. No. 1131844
6 – 7 SiO_2, 49 – 50 B_2O_3, 2.6 – 2.9 Al_2O_3, 6.0 – 14.1 Na_2O, 2.2 – 5.4 K_2O, 3.2 – 11.5 Li_2O, 4.6 – 4.9 CaO, 4.6 – 4.9 BaO	Softening temperature 440 – 480°C	Decreased firing temperature	U.S. patent No. 3615772
41.4 – 48.3 SiO_2, 8.2 – 10.1 Al_2O_3, 13.9 – 17.7 B_2O_3, 0.3 – 0.4 Fe_2O_3, 7.5 – 11.1 ZnO, 6.2 – 8.8 SrO, 3.3 – 5.4 CaO, 0.3 – 0.4 MgO, 2.9 – 3.4 R_2O, 5.0 – 7.4 ZrO_2	Firing temperature 800 – 850°C TCLE 56.2 × 10^{-7} K^{-1}	The same	P. G. Gaprindashvili, M. P. Tsitskishvili, I. V. Dzhakobiya, I. G. Khizanishvili, Ts. P. Tsanava USSR Inventor's Certif. No. 280993
37.40 – 44.06 SiO_2, 5.44 – 5.98 Al_2O_3, 22.64 – 25.10 B_2O_3, 0.09 – 0.13 Fe_2O_3, 7.97 – 8.37 ZnO, 12.16 – 13.28 CaO, 0.06 – 0.08 Na_2O, 1.29 – 1.55 K_2O, 6.1 – 7.9 La_2O_3, 0.19 – 0.21 TiO_2	Firing temperature 990°C TCLE (51.5 – 53) × 10^{-7} K^{-1}	Production of clear glaze	G. K. Gode, L. A. Klyavinya, I. M. Karlson USSR Inventor's Certif. No. 1090670

TABLE 1 (*continued*)

Composition, wt.%	Properties	Specific features	Authors, published source
41.43 – 47.39 SiO_2, 8.64 – 14.23 Al_2O_3, 9.98 – 20.67 B_2O_3, 0.31 – 0.34 Fe_2O_3, 7.35 – 9.05 ZnO, 1.69 – 7.49 CaO, 0.26 – 0.29 MgO, 1.37 – 1.51 Na_2O, 1.28 – 1.41 K_2O, 11.3 – 14.11 ZrO_2	Melting temperature 1300°C Firing temperature 960 – 1100°C TCLE (61 – 62) × 10^{-7} K^{-1} Thermal resistance 300 – 350°C Cold resistance 60 – 65 cycles Abradability 0.012 g/cm^2	Increased cold and abrasion resistance	O. I. Kvitsaridze, G. M. Kakabadze, Ts. P. Tsanava USSR Inventor's Certif. No. 1100260
54.0 – 54.4 SiO_2, 8.56 – 12.58 Al_2O_3, 14.77 – 16.22 B_2O_3, 6.03 – 16.65 CaO, 0.06 – 0.1 MgO, 3.43 – 8.37 Na_2O, 2.08 – 2.96 K_2O, 0.83 – 1.50 Fe_2O_3, 0.20 – 0.41 TiO_2, 0.23 – 0.33 FeO, 0.23 – 0.47 P_2O_5, 0.21 – 0.45 V_2O_5	TCLE (60.43 – 74.7) × 10^{-7} K^{-1} Thermal resistance 520 – 690°C Spreadability 245 – 295 mm	Increased thermal resistance	P. A. Kosobokova, N. Ya. Vasil'eva, N. F. Shcherbana RF patent No. 2112757
25.02 – 32.55 SiO_2, 5.06 – 7.61 Al_2O_3, 26.00 – 31.87 B_2O_3, 2.81 – 4.20 ZnO, 24.15 – 30.26 CaO, 0.23 – 0.36 MgO, 0.74 – 1.13 Na_2O, 0.98 – 1.46 K_2O, 0.13 – 0.19 Fe_2O_3, 0.02 – 0.04 TiO_2, 3.95 – 5.94 ZrO_2, 0.01 – 0.02 MnO	Firing temperature 920 – 950°C Microhardness 50 – 70 MPa Whiteness 50 – 70%	Increased whiteness	A. P. Zubekhin, N. V. Tarabrina RF patent No. 2103245
38.0 – 42.7 SiO_2, 21.5 B_2O_3, 10.0 – 13.4 Al_2O_3, 0.83 – 2.63 ZnO, 0.40 – 0.45 MnO, 4.77 – 5.21 Fe_2O_3, 1.01 – 1.13 MgO, 6.17 – 10.21 CaO, 1.02 – 1.84 BaO, 1.10 – 1.28 K_2O, 4.12 – 6.58 Na_2O, 0.31 – 0.42 TiO_2	Firing temperature 960 – 980°C Firing duration 65 – 70 min TCLE (48.15 – 59.71) × 10^{-7} K^{-1} Microhardness 548 – 590 kgf/mm^2	Increased luster Brown color shade	M. K. Gal'perin, N. A. Mumladze, V. S. Mitrokhin USSR Inventor's Certif. No. 1010030
38 – 48 SiO_2, 20 – 34 B_2O_3, 10 – 15 Al_2O_3, 3 – 6 SrO, 0.1 – 2.0 Fe_2O_3, 0.1 – 1.0 CaO, 0.1 – 3.0 MnO, 4 – 8 Na_2O, 1 – 5 K_2O, 0.5 – 2.5 Li_2O, 0.1 – 0.4 TiO_2, 0.1 – 1.0 WO_3, 0.5 – 2.5 F	Firing temperature 760 – 800°C Optimum firing temperature 920 – 980°C TCLE (50 – 57) × 10^{-7} K^{-1}	Decreased firing temperature	A. P. Raman, L. K. Bil'kenya, D. A. Krade, I. P. Parman, V. É. Shvinka, Yu. Ya. Éiduk USSR Inventor's Certif. No. 416324
	Special purpose low-melting glazes		
2 – 10 SiO_2, 20 – 30 B_2O_3, 34 – 43 ZnO, 30 – 37 BaO	Softening temperature below 660°C TCLE (65 – 95) × 10^{-7} K^{-1} Dielectric constant below 7.5 at frequency 1 MHz at room temperature	Used as plasma display coating	UK patent No. 01100467.8
0.5 – 5.0 SiO_2, 5 – 20 B_2O_3, 60 – 85 Bi_2O_3, 5 – 25 ZnO, 1 – 5 SO_2	Seal formation temperature is lower than transformation temperature of components being sealed TCLE (70 – 100) × 10^{-7} K^{-1}	Lead-free sealing glass for producing two-layer glass absorbing external sound and heat impacts	France patent No. 9906734
44 – 58 SiO_2, 6 – 12 Al_2O_3, 1 – 6 B_2O_3, 0 – 15 ZnO, 1 – 22 CaO	Melting duration 10 – 30 min	Smooth surface Electric resistance does not decrease even in multiple use	Japan patent application No. 5841738
47.4 – 49.0 SiO_2, 13 – 16 Al_2O_3, 13.5 – 15.0 B_2O_3, 11.5 – 15.0 ZnO, 2 – 3 MnO, 7.0 – 7.5 SrO	No data	Increased sealing strength High-strength structures	A. I. Kuznetsov, L. G. Balashova, G. I. Zhuravlev USSR Inventor's Certif. No. 914518
58 – 65 SiO_2, 6.0 – 10.5 B_2O_3, 14 – 25 Al_2O_3, 0 – 9 CaO, 3 – 8 BaO, 0 – 3 MgO, 0 – 2 ZnO	Firing temperature 700°C TCLE (28 – 36) × 10^{-7} K^{-1} Density below 2.6 g/cm^3	Alkali-free glasses are used for thin-layer photo-elements with a locking layer	German patent No. 100008364
56 – 65 SiO_2, 8 – 13 B_2O_3, 8 – 12 Al_2O_3, 8 – 10 CaO, 5 – 12 MgO, 0.5 – 1.0 Na_2O, 0.5 – 1.0 K_2O	Melting temperature 1300 – 1350°C Firing temperature 1150 – 1200°C Firing duration 3 h Thermal resistance 12 thermal cycles Whiteness 87% Luster 78%	Increased whiteness and luster Porcelain coating	N. M. Bobkova, S. A. Gailevich, E. G. Rudakova, I. M. Bykovets USSR Inventor's Certif. No. 1104119

TABLE 1 (*continued*)

Composition, wt.%	Properties	Specific features	Authors, published source
48.0 – 56.4 SiO_2, 19.0 – 23.5 B_2O_3, 3 – 5 Al_2O_3, 2.5 – 8.0 CaO, 0.5 – 2.5 MgO, 0.1 – 1.5 Na_2O, 2.0 – 5.5 K_2O, 0.1 – 1.0 Li_2O, 4.5 – 10.0 ZrO_2	Melting temperature 1410 – 1420°C Firing temperature 820 – 1000°C TCLE $(56 – 56.8) \times 10^{-7}$ K^{-1} Chemical resistance 0.15 – 0.26% Thermal resistance 10 – 12 thermal cycles	Increased chemical resistance Expanded firing interval Used in chemical industry	N. M. Bobkova, S. A. Barantseva, A. G. Smolenskaya, O. N. Beskaraeva, T. I. Mikhal'skaya, L. A. Demishtein, N. P. Poddubnaya USSR Inventor's Certif. No. 1119991
60.7 – 66.8 SiO_2, 10.26 – 12.00 B_2O_3, 2.06 – 2.14 Al_2O_3, 0.39 – 0.42 Fe_2O_3, 8.25 – 12.05 CaO, 0.05 MgO, 11.92 – 14.07 Na_2O, 0.08 – 0.09 K_2O, 0.04 TiO_2	Melting temperature 1250 – 1300°C Firing temperature 1000°C TCLE $(75.92 – 83.44) \times 10^{-7}$ K^{-1} Thermal resistance 500°C	Low production cost due to using recycled waste Porcelain coating	A. E. Buruchenko, L. S. Kolesnikova RF patent No. 2098367
51.40 – 58.00 SiO_2, 6.97 – 9.70 B_2O_3, 8.87 – 9.45 Al_2O_3, 1.45 – 1.66 Fe_2O_3, 17.15 – 22.86 CaO, 0.29 – 0.48 MgO, 1.68 – 2.13 Na_2O	Firing temperature 1040 – 1050°C TCLE 66×10^{-7} K^{-1} Alkali resistance 99.61% Resistance to cold 118 cycles	Increased TCLE, increased frost and alkali resistance Production of caustic and soda	R. S. Krivosheeva, L. S. Opaleichuk, V. F. Pavlov, V. N. Dubatov USSR Inventor's Certif. No. 1025676
26.0 – 34.5 B_2O_3, 0.1 – 0.4 Al_2O_3, 0.7 – 18.0 SiO_2, 7.8 – 10.0 ZnO, 28.5 – 38.0 BaO, 4.5 – 5.0 MgO, 0.1 – 2.2 CaO, 0.1 – 3.6 Na_2O, 5.4 – 6.9 NaF, 3.6 – 4.6 AlF_3	Decreased firing temperature Does not crystallize in working and fusion temperature intervals	Used as enamel for glass and for decoration with colorants added	V. D. Khalilev, L. I. Venzel' USSR Inventor's Certif. No. 1030330
46 – 57 SiO_2, 8 – 15 Al_2O_3, 6.24 – 9.36 B_2O_3, 3.5 – 8.5 ZnO, 0.08 – 0.12 Fe_2O_3, 3.61 – 7.82 CaO, 0.2 – 0.3 MgO, 4.85 – 5.10 Na_2O, 1.5 – 1.9 K_2O, 8 – 13 TiO_2	Firing temperature 950 – 980°C – dull coating Firing temperature 1040 – 1100°C – lustrous coating Thermal resistance 190 – 210°C Cold resistance 35 – 50 cycles	Increased thermal resistance Used for electrotechnical purposes	A. V. Khrudzhe, B. M. Datsenko USSR Inventor's Certif. No. 1058913
39.1 – 45.9 SiO_2, 21.5 – 26.8 B_2O_3, 10.9 – 12.8 Al_2O_3, 1.9 – 3.9 CaO, 1.5 – 2.1 MgO, 1.1 – 4.4 Na_2O, 2.4 – 3.1 K_2O, 2.4 – 3.8 Fe_2O_3, 0.5 – 1.6 MnO_2, 5.9 – 9.1 TiO_2	Melting temperature 1280 – 1300°C Firing temperature 925 – 1020°C Luster formation temperature 840°C TCLE 65×10^{-7} K^{-1} Thermal resistance 19 – 20 thermal cycles	Increased thermal resistance Expanded firing temperature	Ya. K. Klyavin'sh, P. G. Pauksh, P. G. Raman, É. Ya. Permyakov, M. L. Grinberg, Yu. Ya. Éiduk USSR Inventor's Certif. No. 1100258
39.6 – 53.0 SiO_2, 15.7 – 18.7 B_2O_3, 6.6 – 9.5 Al_2O_3, 0.2 – 0.3 Fe_2O_3, 13.1 – 16.0 CaO, 0.5 – 1.3 MgO, 2.6 – 3.6 Na_2O, 0.9 – 1.2 K_2O, 5.5 – 6.9 ZrO_2, 1.9 – 2.6 F_2	Spreading temperature 960 – 970°C TCLE $(58.6 – 62) \times 10^{-7}$ K^{-1} Thermal resistance 250°C Microhardness 68 – 69 MPa Cold resistance 70 cycles	Increased cold and thermal resistance and microhardness	N. M. Bobkova, E. M. Dyatlova, G. Ya. Minenkova, O. I. Yaremchuk USSR Inventor's Certif. No. 1112017
41.30 – 42.85 SiO_2, 15.3 – 16.7 B_2O_3, 2.8 – 5.6 Al_2O_3, 17.4 – 17.9 TiO_2, 1.4 – 1.8 MgO, 12.7 – 16.3 Na_2O, 0.15 – 3.32 K_2O, 0.03 – 0.15 $K_2Cr_2O_7$, 0.72 – 1.50 Fe_2O_3	Firing temperature 800 – 820°C TCLE $(81.1 – 92.5) \times 10^{-7}$ K^{-1}	Increased chemical resistance Stability of cream color	Ya. I. Belyi, S. M. Ponomorchuk, O. I. Bondar Ukraine patent No. 27113
39.66 – 40.38 SiO_2, 19.78 – 21.58 B_2O_3, 6.48 – 6.66 Al_2O_3, 0.7 – 1.7 Fe_2O_3, 0.3 – 0.5 MnO_2, 14.84 – 15.61 SrO, 2.54 – 3.64 CaO, 2.95 – 3.13 MgO, 4.98 – 5.05 Na_2O, 1.95 – 2.02 K_2O, 1.95 – 2.02 ZrO_2, 0.50 – 1.36 F	Firing temperature 1000 – 1100°C TCLE $(61.09 – 61.46) \times 10^{-7}$ K^{-1} Speadability 60 – 70 mm Luster 68 – 75%	Increased firing interval Increased speadability and luster	T. L. Rzhevuskaya, G. V. Tsybul'skaya, L. G. Khodskii USSR Inventor's Certif. No. 1126552
71 – 73 SiO_2, 7 – 10 B_2O_3, 6 – 9 Al_2O_3, 0.5 – 2.0 LiO_2, 0 – 10 Na_2O, 0 – 10 K_2O, 0 – 2 MgO, 0 – 3 CaO, 0 – 3 SO_2, 0 – 3 BaO, 0.3 ZnO, 0 – 1 ZrO_2, 0 – 1 CO_2, 0 – 3 TiO_2, 0 – 1 Fe_2O_3	TCLE $(50 – 57) \times 10^{-7}$ K^{-1}	High chemical resistance Used as sealing glass for iron-cobalt-nickel alloys	German patent application No. 19842942
43 – 46 SiO_2, 11.8 – 18.8 B_2O_3, 5.6 – 11.5 Al_2O_3, 0.4 – 1.6 Fe_2O_3, 0.7 – 10.5 CaO, 0.1 – 4.4 MgO, 1.6 – 2.8 K_2O, 4.7 – 8.8 Na_2O, 2.1 – 8.3 ZnO, 0.1 – 8.0 ZrO_2, 0.1 – 0.3 FeO, 0.02 – 0.15 P_2O_5, 0.4 – 2.1 F, 0.7 – 3.7 TiO_2	Firing temperature 950 – 1080°C TCLE $(54 – 67) \times 10^{-7}$ K^{-1} Spreadability 215 – 264 mm	Increased spreadability Increased firing interval Used in coatings for household and ornamental articles	K. A. Kosobokova RF patent No. 2139259

this case the glaze does not have time to fuse over the emerging funnels and in cooling they become manifested in the form of pinholes. The propensity to pinholes depends on material components and firing conditions of the glaze coating. The number of pinholes can be reduced by using raw materials which do not emit gaseous products at high temperatures, for instance calcined alumina instead of kaolin, or talc instead of dolomite. Adequate drying of the product before firing and good purification of glaze contribute as well to decreasing the number of pinholes.

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